Ab initio Calculations for $SrTiO_3$ (100) Surface Structure

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Abstract. Results of detailed calculations for $SrTiO_3$ (100) surface relaxation and the electronic structure for the two different terminations (SrO and TiO_2) are discussed. These are based on *ab initio* Hartree-Fock (HF) method with electron correlation corrections and Density Functional Theory (DFT) with different exchange–correlation functionals, including hybrid (B3PW, B3LYP) exchange techniques. Results are compared with previous *ab initio* plane wave LDA calculations. All methods agree well on both surface energies and on atomic displacements. Considerable increase of Ti–O chemical bond covalency nearby the surface is predicted, along with a gap reduction, especially for the TiO_2 termination.

INTRODUCTION

Thin films of perovskite ferroelectrics are important for many technological applications, where surface structure and its quality are of primary importance[1, 2, 3, 4]. In this paper, we calculated the relaxed atomic structure of the $SrTiO_3$ surface in the cubic phase. The $SrTiO_3$ (100) surface relaxation has been experimentally studied by means of several techniques, e.g. low energy electron diffraction (LEED), reflection high-energy electron diffraction (RHEED), medium energy ion scattering (MEIS) and surface X-ray diffraction (SXRD) measurements [5, 6, 7, 8, 9]. Several *ab initio* [10, 11, 12, 13, 14, 15, 16, 17] and shell model (SM) [18, 19] theoretical studies were published recently for the (100) surface of $BaTiO_3$ and $SrTiO_3$ crystals. In order to study dependence of the surface relaxation properties on exchange–correlation functionals and localized/plane wave basis sets used in calculations, in this paper we performed a detailed comparative study based on a number of different techniques. Preliminary results are published in Ref. [20].

METHOD

In this study we restrict ourselves to simulations of $SrTiO_3$ in the cubic perovskite phase, with (001) surfaces terminated by a plane containing SrO units, or TiO_2. To simulate both surfaces, we used symmetrical slabs consisting of seven alternating TiO_2 and SrO layers.

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The total energies and electronic structures of these slabs were calculated by several quite different methods: HF with different DFT-type *a posteriori* electron correlation corrections to the total energy [21] such as Generalized Gradient Approximation (HFGGA), Perdew–91 (HFPer91), Lee–Yang–Parr (HFLYP); and full-scale DFT calculations based on the Kohn-Sham equation with a number of exchange-correlation functionals, including Local Density Approximation (LDA), Generalized Gradient Approximation (GGA) by Perdew and Wang (PW), Perdew, Burke and Ernzerhof (PBE), as well as Becke exchange functionals using Becke's three–parameter method, combined with the non–local correlation functionals by Perdew and Wang (B3PW), as those by Lee, Yang, and Parr (B3LYP). For all calculations we used the CRYSTAL–98 computer code (see [22] and references therein for description of all mentioned techniques), in which both (HF/DFT) types of calculations are implemented on equal grounds. Unlike previous plane–wave calculations, this code uses the localized Gaussian-type basis set. In our simulations we applied the standard basis set recommended for $SrTiO_3$ [22]. Another advantage of the CRYSTAL–98 code is its treatment of purely 2D slabs, without an artificial periodicity in the direction perpendicular to the surface, commonly employed in all previous surface–band structure calculations (e. g., [10, 16]). Preliminary analysis of the optimized atomic structure was presented in Ref. [23]. A present study is considerably extended by the analysis of band structure, total and projected density of states, bond populations, and dipole moments characterizing atomic polarization and deformation. In particular, the dipole (d) moments characterize atomic deformation and polarization along the z axis perpendicular to the surface.

For optimization of atomic coordinates through minimization of the total energy per unit cell, we use our own computer code that implements the Conjugated Gradients optimization technique [24] with numerical computation of derivatives. Using this code, we optimized the atomic positions in several top layers of a $SrTiO_3$ slab consisting of seven planes terminated by TiO_2, or by SrO on both sides of a symmetrical slab where both surfaces are either TiO_2 or SrO.

First of all, we have tested how different methods reproduce the experimentally observable bulk properties – the lattice constant a_0 and the bulk modulus B. The LDA calculations underestimate a_0 by 0.8% and overestimate B by 20%. The HF method without any correlation corrections overestimates both a_0 (by 1%) and B (by 16%). HF with GGA corrections makes a_0 too small (by -1.5%), but B even larger (by 41%). Lastly, the hybrid B3PW method gives much better result for B (a discrepancy by 4%) and overestimates a_0 by only 1%. In other words, it is not easy to choose the optimal method reproducing all properties of $SrTiO_3$ equally well, but the hybrid B3PW method is one of the best.

Table 1 presents results for the effective static (Mulliken) charges. The effective charges for Ti and O ions, both in the bulk and on the surface, are much smaller than formal ionic charges (4 e , -2e, respectively). This arises due to the partly covalent nature of the Ti-O chemical bond. In contrast, Sr charge remains close to the formal charge, +2e. Note that these results are very close for all methods used.

The Ti–O chemical bond covalency is confirmed by the bond populations in Table 2, which vary from 0.05 e to 0.11 e, dependent on the particular method. Obviously, there is no chemical bonding between any other types of atoms, e.g. Sr–O or O–O.

Both effective atomic charges and bond populations increase in a series of DFT

TABLE 1. Static charges of atoms calculated for the bulk $SrTiO_3$ by means of variety of DFT and HF methods.

Atom (A)	LDA	B3LYP	B3PW	BLYP	PBE	PWGGA	HF
Sr^{2+}	1.830	1.852	1.852	1.835	1.832	1.834	1.909
Ti^{4+}	2.126	2.325	2.272	2.266	2.206	2.212	2.584
O^{2-}(z)	-1.319	-1.392	-1.375	-1.367	-1.346	-1.349	-1.497

TABLE 2. Bond populations (in milli e) for the bulk $SrTiO_3$. Negative populations mean atomic repulsion. I and II is the first and second nearest neighboring atoms for the bulk oxygen O(I).

Atom A	Atom B	LDA	B3LYP	B3PW	BLYP	PBE	PWGGA	HF
O(I)	O(I)	-48	-36	-36	-30	-32	-34	-40
	Sr(I)	-10	-8	-10	-4	-6	-6	-10
	Ti(I)	52	74	82	66	74	70	112
	O(II)	-2	-4	-4	-2	-2	-2	-8

functionals which increasingly better account for the exchange effects, i.e. LDA–GGA–hybrid functionals– and lastly, HF. The optical band gap usually also increases in the same series. Since vacant orbitals in $SrTiO_3$ are localized on cations, an increase of the band gap leads to an additional transfer of the electron density from cations to anions, accompanied by a growth of ionicity.

We have analyzed different contributions to the Ti–O bond population. It appears that the Ti–O bond population has two contributions: a positive contribution due to chemical bonding of *2p*–orbitals of O ions with *4d*–orbitals of Ti, and a negative contribution as result of repulsion of the same orbitals of O ions from Ti ion *cores* (both *s*– and *p*–orbitals). The positive contribution (chemical bonding) does not change much in a series of calculations with different exchange–correlation functionals. However, the negative contribution decreases significantly, which results in a total increase of the bond population.

MAIN RESULTS FOR SURFACES

Atomic relaxation

Our atomic displacements in the outermost $SrTiO_3$ planes obtained by means of various *ab initio* methods were analyzed recently [23]. We want only to stress here that our Gaussian-basis results are in qualitative agreement with previous plane-wave calculations [10, 16]. Both DFT and HF with correlation effects predict larger Sr displacement on the SrO–terminated surface than that for Ti atom on the TiO_2-terminated surface, also in agreement with previous *ab initio* calculations. For the TiO_2 termination *all* theoretical methods predict the surface O atom to relax inwards, in contrast to the SrO termination. Relaxation of atoms in the third plane is already quite small. In all calculations of the surface energy for SrO termination are slightly smaller than for the TiO_2

termination. However, the energy difference is small and both surfaces thus are energetically nearly equally favorable, in agreement with the experimental observation [5]. Note that the surface energy of 1.37 eV per cell, which was calculated for TiO_2–terminated surface by SM approach [19], is also slightly larger than the surface energy for SrO–termination (1.33 eV/cell). The ab initio LAPW calculations [14] gave similar average surface energies of 1.27 eV per cell.

A comparison of a series of our HF and DFT calculations for the surface rumpling and interatomic distance changes with the two previous ab initio plane-wave studies [10, 16] and classical SM calculations [19] was presented in Ref. [23]. The agreement is quite good for all functionals used. All theoretical methods (both quantum mechanical, irrespective on particular exchange–correlation functional and basis set type, and classical SM) give the same signs for both the rumpling and the change of the interplanar distances. They predict much larger rumpling for the SrO surface in comparison to that for the TiO_2 surface, compression of the distance between the first and second planes, and its expansion for the second and third planes.

Charge distribution

For all methods used the cation charges in the two top layers in the SrO–terminated surface turn out to be smaller than in the bulk. In contrast, the O negative charges in these layers became even more negative, due to additional electron charge transfer. Changes in atomic charges in deeper layers become very small, their sign vary, dependent on the used exchange–correlation functional.

These effects are pronounced more strongly in the case of TiO_2–terminated surface. In particular, charge reduction of surface Ti ions (-0.132 e) is much larger than that on the SrO–terminated surface (-0.027 e). Charges of Sr ions in the subsurface layer of TiO_2-terminated surface are close to Sr charges in the top layer of SrO-terminated surface. In the third layer Ti charges are still reduced, but the magnitude of the charge reduction is relatively small. Sr charges in the central layer of the slab are essentially the same as in the $SrTiO_3$ bulk. In contrast, the O charges are reduced through the entire TiO_2-terminated slab. This O charge reduction is especially large in the top two layers nearby the surface. Tables 3,4 and 5 gives the difference in the charge densities at [001] planes in the $SrTiO_3$ bulk and the (001) surfaces for both terminations.

This is quite usual that ionic charges obtained in quantum-mechanical computations are smaller than formal ionic charges and our calculations is not an exception (Table 2). As a result, [001] planes in the bulk turn out to be charged, with a charge density per unit cell $\sigma_B(SrO) = -\sigma_B(TiO_2)$ (see Table 3). A half of this charge density is donated from the TiO_2 planes to each of the two neighboring SrO planes. If the charge densities of these planes were calculated using formal ionic charges, they would be neutral. This charge redistribution makes the (001) surfaces polar with the dipole moment perpendicular to the surface. (In our slab model this moment disappear due to the symmetry plane.) This is also called "type–III surface", according to generally-accepted classification by Tasker [25], instead of a neutral, or "type–I surface".

Since we neglect defect creation in this study, the only way to stabilize this surface

is to add the compensating charge density $\sigma_B/2$ to the TiO_2-terminated surfaces and -$\sigma_B/2$ to the SrO-terminated surfaces. This additional charge density coincides with the density, which was transfered from the TiO_2 [001] plane to each of its neighboring SrO planes.

The charge density changes with respect to the bulk properties are summarized in Table 4 and Table 5. As one can see, the additional charge is mostly localized on the TiO_2 unit in the first or second plane, dependent on the termination. This is true for all exchange-correlation functionals used for TiO_2 termination, and for most functionals for the SrO termination (except for BLYP and HF). In the latter case the additional charge located at the top SrO layer just a little bit exceeds the additional charge at the subsurface TiO_2 layer. All above–described charge redistribution is in line with ideas of *a weak polarity* [26]. Ion polarization at surfaces with both terminations is significant in the top two planes and becomes very small in deeper layers.

TABLE 3. Charge densities in the (001) crystalline planes of the bulk $SrTiO_3$ (in e, per TiO_2 or SrO unit).

unit	LDA	B3LYP	B3PW	BLYP	PBE	PWGGA	HF
TiO_2	-0.512	-0.459	-0.478	-0.468	-0.486	-0.486	-0.410
SrO	0.511	0.46	0.477	0.468	0.486	0.485	0.412

TABLE 4. Changes in the charge density with respect to the bulk in four top planes (I to IV) of the TiO_2-terminated (001) slab.

unit	LDA	B3LYP	B3PW	BLYP	PBE	PWGGA	HF
TiO_2(I)	0.172	0.142	0.161	0.136	0.156	0.161	0.127
SrO(II)	0.065	0.067	0.059	0.072	0.056	0.066	0.060
TiO_2(III)	0.019	0.020	0.021	0.025	0.030	0.019	0.011
SrO(IV)	0.002	0.001	0.000	0.001	0.000	0.001	0.008

TABLE 5. Changes in the charge density with respect to the bulk in four top planes (I to IV) of the SrO-terminated (001) slab

unit	LDA	B3LYP	B3PW	BLYP	PBE	PWGGA	HF
SrO(I)	-0.061	-0.086	-0.088	-0.112	-0.101	-0.101	-0.096
TiO_2(II)	-0.201	-0.127	-0.128	-0.101	-0.127	-0.127	-0.088
SrO(III)	0.006	-0.014	-0.018	-0.015	-0.012	-0.008	-0.013
TiO_2(IV)	0.006	-0.011	-0.007	-0.014	-0.008	-0.009	-0.013

On the SrO–terminated surface both Sr and O ions have negative dipole moments. This means that their dipole moments are directed inwards to the surface (direction outwards from the surface is chosen as positive). The dipole moments of Sr ions are surprisingly large, only by $\approx$ 30 % less then those for surface oxygen ions. In the subsurface layer of SrO terminated surface Ti atoms also reveal considerable negative dipole moments. These moments are smaller than those of the surface cations by 55 %–65 %. Polarization of Sr ions in the third layer is very small, but still found negative for all used functionals. Polarization of O ions in the subsurface layer, as well as in the next third layer, is also insignificant. For most functionals used the O dipole moments in these layers are negative. The only exception are calculations with LDA and B3LYP functionals giving the positive dipole moments for the subsurface O ions, and LDA calculations for O ions in the third layer. However, these effects are very delicate since dipole moments are very small.

On the TiO_2–terminated surface polarization of cations has an opposite sign than on the SrO-terminated surface: surface Ti ions now reveal positive dipole moments. The polarization value is approximately the same but with an opposite sign as compared with subsurface Ti for the SrO-termination. Dipole moments on the subsurface Sr ions are small but also positive. In the third layer the dipole moments on Ti ions turn out to become negative (for all methods except HF calculations). Oxygen polarization on the TiO_2–terminated surface is surprisingly small.

In the surface layer calculated O dipole moments are negative for most functionals, except for PBE and PWGGA. These moments become positive on the subsurface O ions and, again, negative on the O ions in the third layer. *Bond populations* between atoms for TiO_2 termination are given in Table. 6. Let us, for the analysis

TABLE 6. The bond populations (in me) for TiO_2 termination. I to IV are number of planes enumerated from the surface.

Atom A	Atom B	LDA	B3LYP	B3PW	BLYP	PBE	PWGGA	HF
O(I)	O(I)	-36	-28	-30	-24	-26	-26	-34
	Ti(I)	108	124	128	114	118	114	146
	Sr(II)	-10	-10	-10	-4	-4	-6	-28
	O(II)	-20	-16	-16	-10	-8	-10	-36
O(II)	Ti(I)	100	132	124	128	120	118	150
	O(II)	4	2	2	2	2	2	2
	Sr(II)	-8	-8	-10	-4	-4	-6	-20
	Ti(III)	78	92	92	84	86	88	104
	O(III)	-38	-30	-32	-24	-24	-26	-42
O(III)	Sr(II)	-4	-4	-6	0	-2	-2	-18
	O(III)	-42	-34	-36	-30	-30	-32	-44
	Ti(III)	62	86	86	76	78	74	114
	Sr(IV)	-8	-8	-10	-4	-4	-6	-22
	O(IV)	-46	-36	-34	-30	-18	-20	-44
O(IV)	Ti(III)	54	78	80	68	72	70	106
	O(IV)	4	2	2	2	2	2	2
	Sr(IV)	-10	-8	-10	-4	-30	-6	-22

take the particular B3PW results. The major effect observed here is strengthening of the Ti–O chemical bond near the surface, which is already pronounced in the bulk (Table 2), where the Ti–O bond is considerably populated (82 me, m=milli). The Ti–O bond population for the TiO_2– terminated surface is 128 me, which is about 50 % larger than the relevant values in the bulk. The Ti-O populations in the direction perpendicular to the surface, i.e. between Ti and O atoms in the first and second, the second and third plane, and lastly, the third and fourth planes (124 me, 92 me, and 86 me) also exceed the bulk value. In contrast, the Sr–O populations are very small and even negative which indicates the repulsion. (The same is true for O-O interactions.) This effect is also well seen from the Sr effective charges, which is close to the formal ionic charge of +2e. Calculated total electron densities confirm the Ti–O covalency effects discussed above, whereas the difference electron density maps calculated with respect to the superposition density for Sr^{2+}, Ti^{4+}, and O^{2-} ions, demonstrate considerable charge density redistribution for both $SrTiO_3$ surface terminations. These maps show that there is no trace of covalent bonding between Sr and O atoms. The Sr atoms nearest the surface are polarized. Their electronic density is shifted inwards the bulk in the case of the TiO_2-terminated

surface and outwards on the SrO-terminated surface. For both terminations the nearest the surface Ti-O bond becomes stronger, but the next nearest bond becomes weaker.

Band structure

The values of direct and indirect optical gaps calculated by means of the hybrid B3PW method are summarized in Table 7. The calculated upper valence band for the $SrTiO_3$ bulk is quite flat, with the top at M and R points of the Brillouin zone, and almost perfectly flat upper valence band between these points. The bottom of the lowest conduction band lies at the Γ point, with very close energy to the X point. The dispersion curve between these Γ and X points is very flat. Such flat bands could make possible hole and exciton self-trapping. An exciton self-trapping in $SrTiO_3$ bulk was indeed discussed quite recently [27].

The optical bulk gap obtained with the hybrid B3PW method is 4.16 eV, to be compared with the experimental value of 3.3 eV. This corresponds to much better agreement than in the case of typical considerable overestimate of the gap in "pure" HF calculations, or great underestimate in LDA calculations (1.85 eV [10]). The upper valence band consists of O 2p atomic orbitals with a small admixture of orbitals of Ti atoms, whereas conduction band bottom consists essentially of Ti orbitals. Orbital contribution from Sr atoms is negligible in this energy range. The Sr orbitals make a significant contribution to the DOS only at energies much higher in the conduction band.

The top of the upper valence band for the TiO_2-terminated slab is located at the M point of the Brillouin zone. At this point the valence band is split off by more than 1 eV from other valence bands. Analysis of contributions to the density of states shows that this band consists mainly of orbitals belonging to the surface O ions and can be considered as a band of surface states. Other upper valence bands are formed predominantly by 2py orbitals of the surface O atoms. These orbitals are directed along the Ti-O-Ti bridge.

TABLE 7. The calculated B3PW optical gap (in eV) for the bulk and surface-terminated $SrTiO_3$. Experimental bulk gap is 3.3 eV.

	Direct gap					Indirect gap
	Γ	X	M	R	Γ-M	Γ-R
Bulk	4.43	5.08	6.45	7.18	4.23	4.16
SrO	4.12	4.70	5.94		3.71	
TiO_2	3.78	4.38	5.04		3.09	

The lowest conduction band is flat between the Γ and X points. This looks very similar to the case of the bulk crystal. The DOS at the very bottom of conduction band contains contributions from internal Ti ions in the slab. The orbitals of the surface Ti ions contribute to the next lowest conduction bands at higher energy.

The indirect optical gap is reduced from 4.16 eV for the bulk down to 3.09 eV. The main contribution to this reduction comes from the split-off the surface valence band from internal valence bands at the M point. Surface valence and conduction bands are shifted up in energy, what is caused by a decrease of the electrostatic potential at the

surface. As a result, the net electron density on the surface atoms is also reduced and the surface gets a positive charge.

Similar effects but with opposite sign are observed for the SrO-terminated slab. The top of the upper valence band is still at the M point but now the upper band is formed from orbitals of internal O ions. The states located on the surface O ions essentially overlap in energy with the band of valence states. The conduction band created by orbitals of subsurface Ti ions is the lowest in energy conduction bands near the G point. Again, reduction of the indirect band gap stems mainly from a shift of the surface states, but from a shift of the surface conduction band. As a result, the band gap in the SrO-terminated slab becomes 3.71 eV. The electrostatic potential at the SrO-terminated surface increases, which causes lowering of energy of the surface bands, and an increase of the electronic density nearby the surface.

Summing up, the band gap reduction for the TiO_2 termination is considerably larger than for the SrO-termination, in agreement with a qualitative trend obtained in earlier plane wave LDA calculations [10].

CONCLUSIONS

A comparison of ab initio HF and DFT calculations employing different exchange-correlation functionals and localized/plane wave basis sets clearly demonstrates their good agreement for the rumpling and the relative displacements of the second and third planes nearby the $SrTiO_3$ surface. Further comparison of ab initio calculations corresponding to 0 K with experiments performed at room temperature needs a detailed analysis of anharmonic vibrations of the surface atom (especially, Ti). On the other hand, several diffraction experiments used so far clearly contradict each other. This could arise due to both difference in sample preparations and as a result of the different interpretations of indirect experiments.

At the M point we observe a split–off of the surface states from the valence band due to reduced electrostatic potential in the TiO_2–terminated surface and similar split-off the surface states from the conduction band at Γ point in the SrO-terminated surface. This effect, well known in ionic solids under the name of the Tamm states, could stimulate hole migration in the valence band or electrons in the conduction band (depending on the surface termination) to the surface and increase of its catalytic activity.

Our ab initio calculations indicate considerable increase of the Ti–O bond covalency near the surface. This should have impact on the electronic structure of surface defects (e.g., F centers), as well as affect an adsorption and surface diffusion of atoms and small molecules relevant in catalysis.

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